Perturbation approach to the computer simulation of dipolar fluids

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The long range nature of the dipolar potential ϕ has made computer simulation of molecules with electric dipoles highly troublesome. We propose for such calculations a generalization of the Ceperley–Chester procedure for Coulomb fluids [Phys. Rev. A **15**, 755 (1977)], separating ϕ into short range and long range parts, $\phi_{\rm SR}$ and $\phi_{\rm LR}$. The reference system with $\phi_{\rm SR}$ interaction can be studied using standard simulation methods for truly short range potentials. The corrections for $\phi_{\rm LR}$ are then incorporated through solution of the reference-hypernetted chain equation. An illustrative calculation shows the correction procedure to be computationally reliable.

I. INTRODUCTION

Numerical simulations of many-body systems are limited of necessity to rather small samples. When the potential is such that a molecule at the center of the finite sample has negligible interaction with one at the boundary, this limitation is essentially removed by the standard technique of periodic replication of the sample throughout space and truncation of the potential.[1] For long range potentials such as Coulomb and dipolar, however, more elaborate remedies must be used if the sample size is to be kept manageable. One such is the Ewald summation over periodic images, pioneered by Brush, Sahlin, and Teller[2] for Coulomb fluids and generalized for the dipolar potential by De Leeuw, Perram, and Smith.[3] Another, also for dipoles, is the reaction field method proposed by Barker and Watts,[4] in which the potential is truncated but the neglected interactions beyond the truncation sphere are approximately accounted for by the reaction field of a surrounding polarizable dielectric medium. In both these cases, special formulas[3,5,6] must be worked out to connect the dielectric constant ϵ with the computed dipole moment fluctuations of the finite sample so as to approximate the value of ϵ for an infinite sample. There may, nonetheless, still be significant dependence on sample size as well as, in the Ewald case, peculiar correlation effects.[1] Furthermore, as noted particularly by Stell *et al.*,[7] while the dielectric constant obtained by these methods can indeed be representative of that of bulk samples, the same is not true of the space correlation functions. These will differ fundamentally from the infinite sample versions in their long range behavior. It is thus of some interest to explore alternative ways of simulating dipolar fluids that are less subject to these analytic deficiencies. In this note, we examine a procedure, based on the reference-hypernetted chain (RHNC) integral equation,[8] that allows use of the simple expedients available for simulation of systems with truly short range potentials yet guarantees the correct asymptotic behavior of the correlation functions.

The method is a straightforward generalization of the procedure first proposed and used by Ceperley and Chester[9] for Coulomb fluids. Briefly, the long range potential of interest, here the radial part of the dipole–dipole interaction

$$\phi(r) = -\mu^2/r^3, \tag{1}$$

is separated into short range and long range parts,

$$\phi(r) = \phi_{\rm SR}(r) + \phi_{\rm LR}(r) \tag{2}$$

with the feature that $\phi_{\rm LR}(r)$ follows the long range form of $\phi(r)$ but contains no singularity at short range. One computes the properties of the reference fluid with potential $\phi_{\rm SR}(r)$ by means of computer simulation using the simplest potential truncation scheme (minimum image or spherical cutoff[1]). Corrections for the long range perturbation $\phi_{\rm LR}(r)$ are then incorporated through the RHNC equation, which builds in the qualitatively exact asymptotic behavior for the correlation functions and permits the use of standard formulas for ϵ in infinite systems.[7]

More specifically, for the short range reference potential to be studied with standard simulation techniques we propose

$$\phi_{\rm SR}(r) = -\frac{\mu^2}{r^3}\frac{4}{\sqrt{\pi}}\int_{r/\lambda}^{\infty} dx\, x^2 e^{-x^2} = -\frac{\mu^2}{r^3}\left[\operatorname{erfc}\left(\frac{r}{\lambda}\right) + \frac{2}{\sqrt{\pi}}\frac{r}{\lambda}\exp\left(-\frac{r^2}{\lambda^2}\right)\right], \tag{3}$$

where λ is a disposable range parameter to be chosen so that

$$\phi_{\rm SR}(L/2) \ll 1 \tag{4}$$

with L the edge length of the sample cube. Equation (3) is the generalization of the Ceperley–Chester choice for the Coulomb version[9] and like it also the same as the lowest-order spherically symmetric part of the Ewald–Kornfeld potential.[3]

In the next section, we examine the procedure for computing the RHNC corrections for the long range potential $\phi_{\rm LR}$. No computer simulation results for the reference system are reported in this work. Instead, to illustrate the feasibility of the approach, we apply the correction to reference system data generated from a solution of the RHNC equation for $\phi_{\rm SR}$. The corrected results then obtained are compared in turn to the corresponding RHNC solution for the *full* potential $\phi(r)$.[10] The two sets of results should of course be identical. What we test in this way is the numerical reliability of the correction procedure, particularly the reconstruction of the reference pair distribution function from a few spherical harmonic coefficients. For molecular potentials with strongly anisotropic core, this is a dubious practice.[11] Here however the potential discontinuity is isotropic. No special problems are encountered and the agreement in end results is very good.

II. RHNC CORRECTION

The formal ingredients for the perturbation correction of a molecular fluid are readily written down.[12] We start with the Ornstein–Zernike (OZ) equation in Fourier transform representation

$$\tilde{S}(12) = \rho \int d\omega_3\, \tilde{C}(13)[\tilde{S}(32) + \tilde{C}(32)] \qquad (5)$$

and the exact closure

$$C(12) = g(12) - 1 - S(12)\,, \qquad (6)$$

$$g(12) = \exp[-\beta\phi(12) + S(12) + B(12)]\,. \qquad (7)$$

Here $\phi(12)$ is the full molecular potential, $g(12)$ and $C(12)$ the pair distribution and direct correlation functions, and $B(12)$ the bridge function or sum of bridge graphs. The series function $S(12)$ is the key quantity in a calculation; like the others, it depends generally on the center of mass separation $\mathbf{r}_{12}$ between two molecules and on their respective orientations ω_1 and ω_2,

$$S(12) = S(\mathbf{r}_{12}, \omega_1, \omega_2)\,. \qquad (8)$$

This and other molecular fluid functions can be expanded in spherical harmonics; orienting the z axis along $\mathbf{r}_{12}$ yields the simplest form,[12]

$$S(12) = 4\pi \sum_{l_1, l_2, m} S_{l_1 l_2 m}(r_{12}) Y_{l_1 m}(\omega_1) Y_{l_2 \bar{m}}(\omega_2)\,, \qquad (9)$$

while setting the z axis along $\mathbf{k}$ similarly gives

$$\tilde{S}(12) = 4\pi \sum_{l_1, l_2, m} \tilde{S}_{l_1 l_2 m}(k) Y_{l_1 m}(\omega_1') Y_{l_2 \bar{m}}(\omega_2')\,. \qquad (10)$$

An identical set of equations is written for the reference system with potential $\phi_{\rm SR}(12)$ constructed using Eq. (3). The difference functions

$$\Delta S(12) = S(12) - S_{\rm SR}(12) \qquad (11)$$

and so on, then become the objects of the perturbation correction, which we can now formulate.

We assume that a computer simulation has generated a sufficient number of coefficients of $g_{\rm SR}(12) = 1 + h_{\rm SR}(12)$ and $\tilde{h}_{\rm SR}(12)$. (Coefficients of the pair distribution function are of course routinely computed in machine simulations, but the transforms generally are not. There appears to be no fundamental problem to doing so, however. This is further discussed below.) From Eqs. (6) and (7) and their short range counterparts we then get

$$\Delta C(12) = g_{\rm SR}(12)\{\exp[-\beta\phi_{\rm LR}(12) + \Delta S(12)] - 1\} - \Delta S(12)\,, \qquad (12)$$

where $g_{\rm SR}(12)$ is to be reconstructed from its coefficients, $\Delta S(12)$ is the object of the calculation, and we have neglected $\Delta B(12)$, which constitutes the RHNC approximation.[8]

The second equation coupling $\Delta C(12)$ and $\Delta S(12)$ is obtained from the OZ equation. Expressed in terms of coefficients as in Eq. (10), Eq. (5) becomes

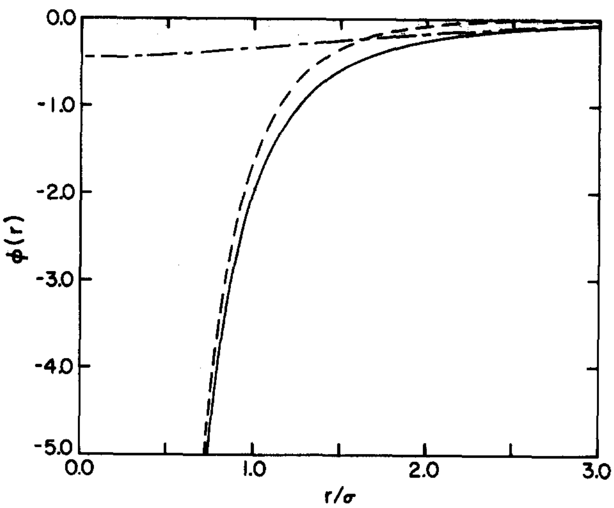

FIG. 1. The radial part $\beta\phi(r) = -\beta\mu^2/r^3$ (solid line) of the dipolar potential and its decomposition into short range (dashed line) and long range (dot–dashed line) parts using Eq. (3) with $\beta\mu^2/\sigma^3 = 2.0$ and $\lambda/\sigma = 1.5$.

$$\tilde{\mathbf{S}}_m(k) = (-1)^m \rho \tilde{\mathbf{C}}_m(k)[\tilde{\mathbf{S}}_m(k) + \tilde{\mathbf{C}}_m(k)]\,, \qquad (13)$$

where $\tilde{\mathbf{S}}_m(k)$ is a matrix with elements $\tilde{S}_{l_1 l_2 m}(k)$, $l_1, l_2 \geqslant m$. With a similar equation for the reference system, we then find, after some algebra,

$$\begin{aligned}\Delta\tilde{\mathbf{S}}_m(k) = \{&\mathbf{I} - [\mathbf{I} + (-1)^m \rho \tilde{\mathbf{h}}_m^{\rm SR}(k)] \\ &\times (-1)^m \rho \Delta\tilde{\mathbf{C}}_m(k)\}^{-1} \\ &\times [\mathbf{I} + (-1)^m \rho \tilde{\mathbf{h}}_m^{\rm SR}(k)]\Delta\tilde{\mathbf{C}}_m(k) \\ &\times [\mathbf{I} + (-1)^m \rho \tilde{\mathbf{h}}_m^{\rm SR}(k)] - \Delta\tilde{\mathbf{C}}_m(k)\,. \qquad (14)\end{aligned}$$

Equations (12) and (14) are to be solved iteratively for $\Delta S(12)$, with which we can then reconstruct the full $g(12)$ and $\tilde{h}(12)$. The method of solution is entirely similar to that of earlier works[10,13] and needs no further discussion here. As noted earlier, the essential givens are the coefficients of $g_{\rm SR}(12)$ and $\tilde{h}_{\rm SR}(12)$.

To illustrate the correction procedure, we have obtained these coefficients using the RHNC equation for a reference hard sphere, *short range* dipolar fluid with density ρ and dipole moment μ specified by $\rho\sigma^3 = 0.8$ and $\beta\mu^2/\sigma^3 = 2.0$, where σ is the hard sphere diameter. The short range potential $\phi_{\rm SR}(r)$ defined by Eq. (3) with $\lambda = 1.5\sigma$ is shown in Fig.

TABLE I. Thermodynamics of the reference system using $\phi_{\rm SR}(12)$ and the RHNC-corrected values for the dipolar hard sphere fluid with $\phi(12) = \phi_{\rm SR}(12) + \phi_{\rm LR}(12)$. The last row gives the "exact" values obtained *directly* from the RHNC equation (Ref. 10). All entries are for $\rho\sigma^3 = 0.8$ and $\beta\mu^2/\sigma^3 = 2.0$.

	Short range system				Corrected values				
λ	No. of coeff.	$\beta U/N$	$\beta p/\rho$	$\rho kT\chi$	No. of coeff.	$\beta U/N$	$\beta p/\rho$	$\rho kT\chi$	ϵ
1.0	13	−0.936	7.36	0.0391	13	−2.61	5.96	0.0416	31.8
1.5	13	−1.80	6.73	0.0403	13	−2.61	5.96	0.0416	31.9
1.5	7	−1.80	6.73	0.0403	13	−2.61	5.96	0.0416	31.7
0					13	−2.61	5.96	0.0416	31.8

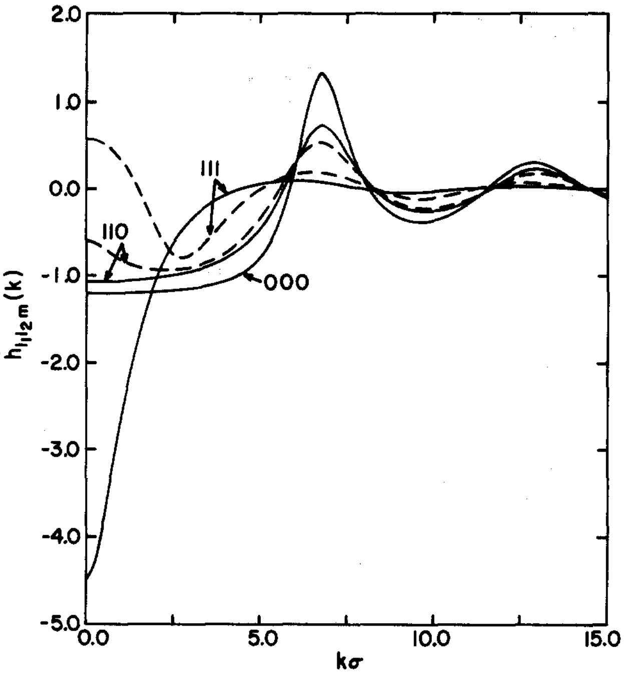

FIG. 2. Harmonic coefficients of $\tilde{h}(12)$ for the short range reference potential (dashed line) and the RHNC-corrected coefficients for the full hard sphere dipolar potential (solid line) at $\rho\sigma^3 = 0.8$ and $\beta\mu^2/\sigma^3 = 2.0$.

1, along with the full potential $\phi(r)$ from Eq. (1) and the long range tail $\phi_{LR}(r)$. It is clear that $\phi_{SR}(r)$ could be safely truncated at ranges usually reached in simulation samples.

The computed internal energy U, pressure p, and compressibility χ for the reference system are listed in Table I for two range parameters λ, to which they are clearly very sensitive. However, the corrected values from the solution of Eqs. (12) and (14) are identical in the two cases, and are identical also to those of the direct RHNC solutions for the full potential $\phi(r)$.[10] This latter agreement suggests that the correction procedure is numerically reliable, though it is not, of course, a test of accuracy of the RHNC approximation itself. Changing the number of short range coefficients used from 13 to just 7 has no effect on these results, as seen in the third row of the table. Finally, the dielectric constant ϵ obtained with the standard infinite-system formulas[7] after correction of the distribution functions is also shown in Table I. Again, the agreement among all the solutions is very good.

The short range behavior of the reference and corrected pair distribution function $g(12)$ is unremarkable. To illustrate the difference in long range behavior, we show in Fig. 2 the first few coefficients of $\tilde{h}(12)$ for both cases. Here we find that the reference system transforms $\tilde{h}^{SR}_{110}(k)$ and $\tilde{h}^{SR}_{111}(k)$ display at very small k at anomalous form somewhat like that found for the reaction field potential,[10] a reflection of the anomalous long range range behavior of the space distribution functions. The algorithm[10,13] for solving the correction equations, however, automatically generates the proper long range tails, so that, e.g.,

$$h^{112}(r) \sim 1/r^3, \tag{15}$$

resulting in the corrected forms of the transforms seen in Fig. 2.

These results were obtained on a grid of 512 points with an interval $\Delta r = 0.02\sigma$. Other details of the calculation are as described in Ref. 10.

Finally, we recall that in a numerical simulation the coefficients of $g_{SR}(12)$ are computed as ensemble averages.[14] The same sort of calculation, using

$$\tilde{g}^{SR}_{l_1l_2m}(k) = \frac{4\pi}{N\rho}\left\langle \sum_{\substack{i,j\\(i\neq j)}} \exp(i\mathbf{k}\cdot\mathbf{r}_{ij})\, Y^*_{l_1m}(\omega_i)\, Y^*_{l_2\bar{m}}(\omega_j) \right\rangle, \tag{16}$$

appears feasible for the transforms, though undoubtedly more time consuming than the one for the spatial coefficients. [The direction of $\mathbf{k}$ in Eq. (16) is along the z axis, so that the ω_j are the conventional (θ_j,ϕ_j) sets.] Finally, as noted by Ceperley and Chester[9] in the Coulomb version, both sets of computed reference system coefficients, for $g(12)$ and for $\tilde{h}(12)$, will have to be extended, smoothed, and made mutually consistent for use in the perturbation calculation.

ACKNOWLEDGMENT

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